NASA-TM-111756

# THERMODYNAMIC ANALYSIS FOR THE COMBUSTION SYNTHESIS OF SiC-$B_4C$ COMPOSITES

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## Introduction

A significant amount of attention has been focussed recently on the development of new structural materials for aerospace, nuclear, armor and energy related applications. These materials should have high melting points, low density, good strength and toughness, and good oxidation and thermal shock resistance. A number of monolithic as well as whisker and fiber reinforced refractory carbides e.g., SiC, $B_4C$ etc. have been actively considered for the above applications [1-6]. In a comprehensive review paper, Thevenot [4] discussed the current status of fabrication and various applications of monolithic boron carbide materials. Schwetz et al. [7] have indicated that SiC-$B_4C$ composite materials would have a combination of desirable mechanical and thermal properties. These include the strength, oxidation and thermal shock resistance of silicon carbide combined with the low density, hardness and wear resistance of boron carbide.

Kobayashi et al [8] have reported the processing conditions and properties of a number of carbon, graphite and refractory carbide (TiC, NbC, TaC etc.) particulate reinforced boron carbide composites produced by hot pressing and pressureless sintering. A number of these composites appear to show good properties for bearings and mechanical seals for high temperature applications as well as for machine parts in contact with some molten metals. In order to have wide application of these materials, innovative and cost-effective processing approaches are needed to produce materials with the desired microstructure and properties in near-net and complex shapes.

Self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) has been used to produce a variety of refractory borides, carbides, nitrides, and silicides containing ceramics and composite materials [9]. The underlying basis for this synthesis is the ability of highly exothermic reactions to sustain themselves in the form of a reaction or combustion wave. The rate of combustion wave propagation can be very rapid (~ 25 cm/s) and can reach temperatures as high as 5000 K [9]. In the CS process, reactions with extremely large thermal gradients (~ $10^5$ K/cm) can be obtained under adiabatic conditions. There are two basic modes of reaction used in combustion synthesis. One spreads mainly by propagation of combustion waves through the reactants which are heated at one end by thermal or laser energy and the reaction self-propagates [9]. Another approach involves the heating of the entire specimen to a temperature at which the reaction becomes spontaneous and takes place simultaneously in the whole specimen. Combustion synthesis is an energy efficient and cost-effective processing approach for producing near-net shape components.

Silicon carbide (SiC) - boron carbide ($B_4C$) composites with interconnected network of SiC and $B_4C$ phaseshave been fabricated by the combustion hot pressing (CHP) technique [10]. A literature review of earlier work indicates lack of a detailed thermochemical understanding of the various processes in the SiC/$B_4C$ system. Thermodynamic calculations can provide a basis for developing energy efficient processing schemes and provide useful information about the stability and occurrence of various phases in the final product.

In this paper, thermodynamic analysis for the combustion synthesis of SiC-$B_4C$ composites are reported. The effects of initial temperature of reaction and the addition of filler phases (SiC and $B_4C$) on the adiabatic temperatures are discussed.

## Thermodynamic Considerations

Combustion synthesis reactions are highly exothermic in nature and once initiated, are self-sustaining without additional energy. The driving force for a process to take place is given by the change in the Gibbs free energy. For solid state reactions, $\Delta H^o$ is a good measure of the change in free energy ($\Delta G^o$) because the change in the entropy ($\Delta S^o$) is usually only of the order of 0.001 kJ $deg^{-1}$ $mol^{-1}$. It should therefore be possible to use heat of formation to predict phase formation sequence when activation or nucleation barriers don't exist. This is due to the fact that a system would always want to go to its lowest possible free energy state. One has to consider, however, the formation of liquid reaction products and modify the calculation accordingly. Frequently, it is of interest to suppress liquid formation by adding an inert diluent substance.

The degree of exothermicity of reaction is characterized by the value of the adiabatic temperature ($T_{ad}$). The adiabatic temperature can be calculated from the following relationship:

$$\Delta H_{T_0} = \int_{T_0}^{T_{ad}} C_p dT \tag{1}$$

where $\Delta H_{T_0}$ is the enthalpy of reaction at $T_0$ and $C_p$ is the combined heat capacity of the products. If the reaction products undergo any phase change below $T_{ad}$, changes in enthalpy and heat capacity have to be made accordingly. For example, if one of the reaction products is in the molten state, then the enthalpy of reaction is

$$\Delta H_{T_0} = \int_{T_0}^{T_m} Cp_s dT + \Delta H_m + \int_{T_m}^{T_{ad}} Cp_l dT \tag{2}$$

where $\Delta H_m$ is the latent heat of fusion and $Cp_l$ is the heat capacity of molten phase. Thermodynamic data for the calculations have been taken from Barin and Knacke [11].

## Results and Discussion

The primary reaction for combustion synthesis is considered starting from the elemental powders. The reaction is as follows:

$$Si + 4\,B + 2\,C = SiC + B_4C \tag{3}$$

The effect of initial temperature of reaction on the adiabatic temperature is given in Fig. 1. The data for the combustion synthesis of SiC and $B_4C$ are provided for comparison. The adiabatic temperature for the formation of equimolar SiC-$B_4C$ composite is 1264 K for an initial temperature of 298 K while for pure SiC and $B_4C$ it is 1775 K and 1038 K, respectively. The adiabatic temperatures for SiC-$B_4C$ composite synthesis are between the SiC and $B_4C$ adiabatic temperatures.

In chemical reactions where exothermicity is very low, a self propagating combustion reaction can not be initiated at room temperature. As an empirical rule for reactions leading to refractory materials, $T_{ad}$ should be around 2100-2300 K to achieve self propagating combustion [9]. For an initial temperature of 1500

K, the calculated adiabatic temperature of equimolar $SiC-B_4C$ system is 2233 K. An initial processing temperature of about 1500 K will be needed to start the combustion reactions. Panek [9] has observed exotherms in the DTA analysis of powder mixtures in the Si-B-C system in the temperature range of 1533-1673 K. In addition, he also observed combustion reactions during the hot pressing of powders in the temperature range of 1573-1673 K. Our theoretical predictions of initial temperature to get combustion reactions agree very well with his experimental results. At lower initial processing temperatures, the chemical reaction was incomplete [9].

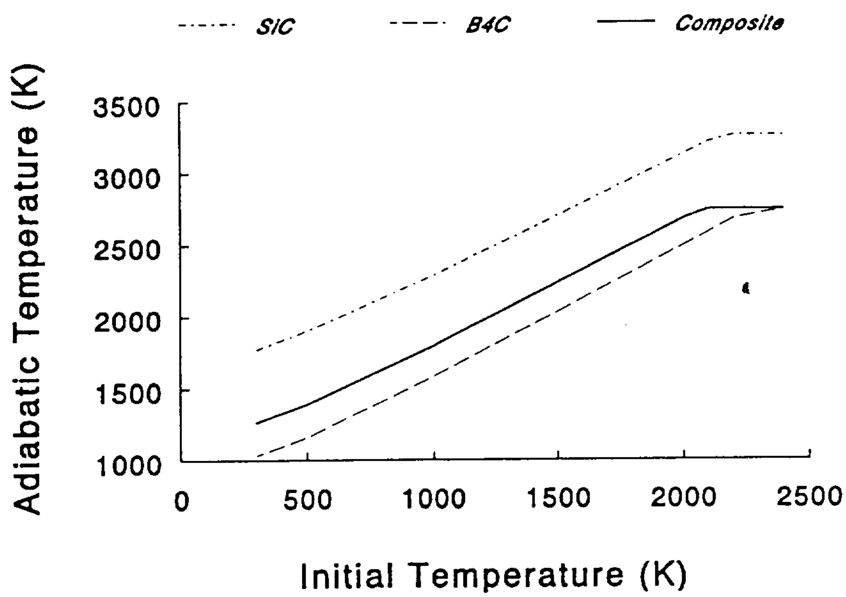


Fig. 1 : **Effect of initial reaction temperature on the adiabatic temperature ($T_{ad}$) of SiC, $B_4C$, and $SiC/B_4C$ composite.**

The adiabatic temperature of reaction (equation 3) as a function of heat of reaction at three temperatures is given in Fig. 2. The heat of reaction (Q) for this reaction is -33.6 kcal/mole. If the initial temperatures for the synthesis are higher than 2050 K, then liquid phase is present in the reaction product.

The presence of fillers has been known to reduce the adiabatic temperature of reactions during combustion synthesis. In Fig. 3, the effect of various amounts of SiC and $B_4C$ fillers on the adiabatic temperature of reaction is given at two initial temperatures (1600 and 2000 K). It is clear from the data that $B_4C$ is a more effective filler than SiC for reducing the adiabatic reaction temperature. It can be seen from this figure that about one mole of $B_4C$ addition reduces the $T_{ad}$ by about 250 K. This suggests the possibility of reducing the adiabatic temperature and controlling the amount of molten fraction by adding diluent phase.

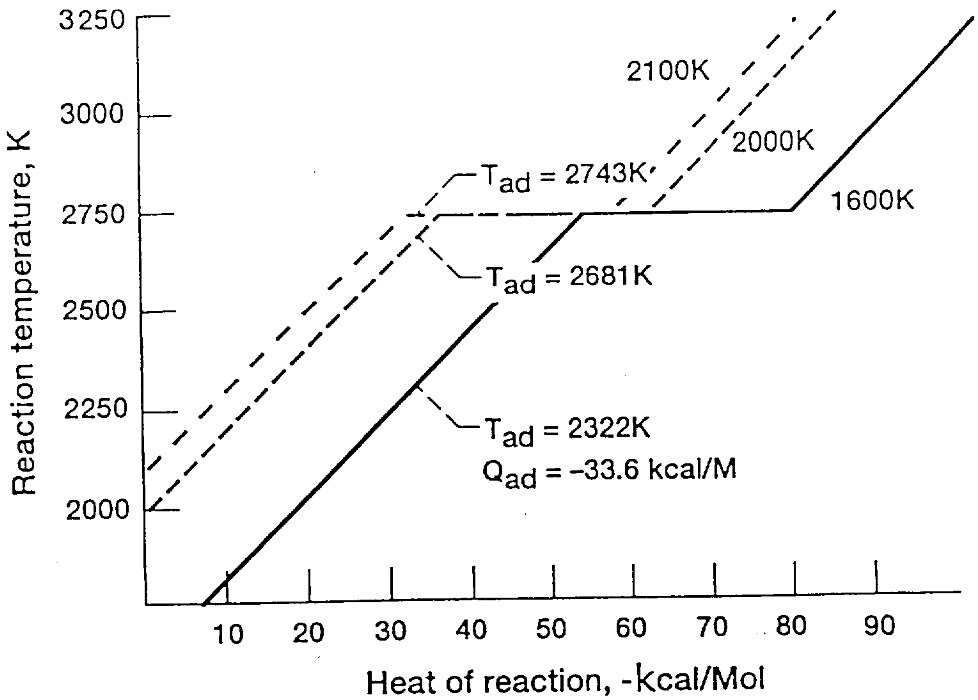


Fig. 2 : Plot of reaction temperature vs heat of reaction for reaction (3) at 1600, 2000, and 2100 K initial temperatures.

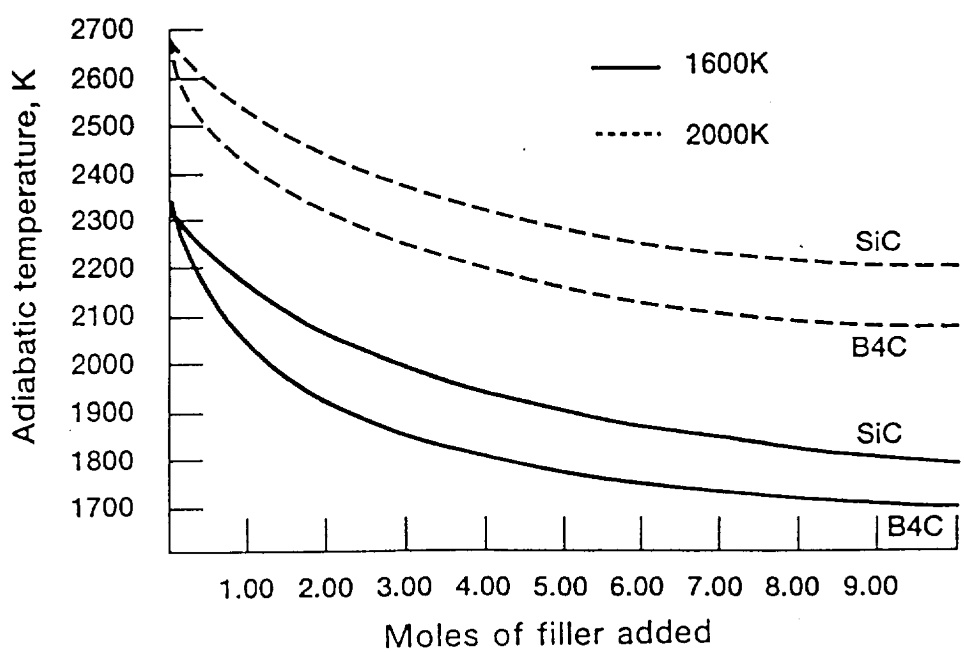


Fig. 3 : Effect of $B_4C$ and SiC addition to reactant mixture on the adiabatic temperature of reaction (3) at 1600 and 2000 K initial temperatures.

Using the densities and atomic/molecular weights of reactants and products (equation 3), reduction in molar volume for this reaction has been calculated to be about 10%. Hot pressing has to be carried out during combustion synthesis in order to achieve fully dense final materials.

Under actual processing conditions, there may be some impurities in the starting powders which may form silicides and other compounds. These compounds can also be incorporated in thermodynamic calculations. In addition, there is solubility of boron in silicon carbide. In order to maintain the stoichiometry of the above reaction, excess boron should be added in the starting reaction mixture.

## Conclusions

The thermodynamic analysis of SiC-$B_4C$ system indicates that the adiabatic temperatures in the combustion synthesis can be reduced significantly by the addition of filler (SiC, $B_4C$) phases. The $B_4C$ phase is much more effective in reducing the adiabatic temperature than SiC. These parameters can be very helpful in the selection of optimum processing conditions for the synthesis and densification of SiC-$B_4C$ composites.

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